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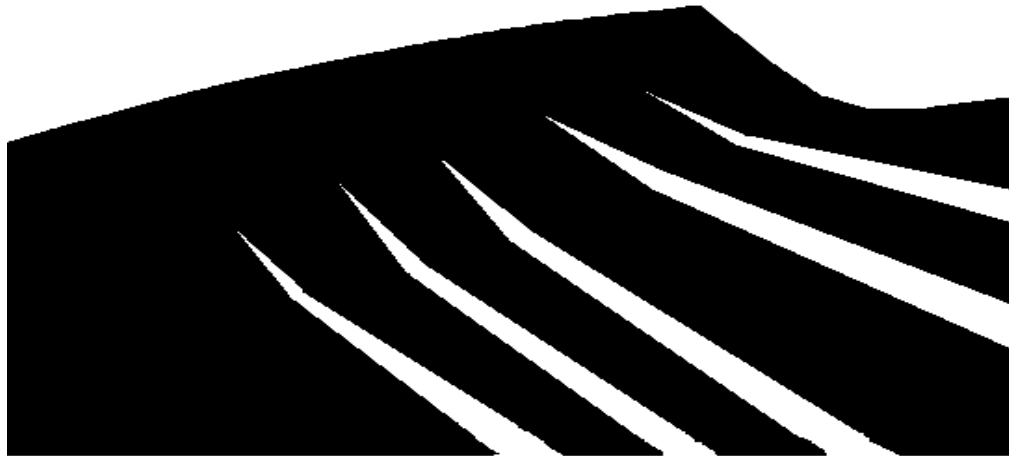
August 16, 1996

LANL-CST-DP-95, R2

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PREPARATION OF SAMPLES FOR CHLORINE-36 ANALYSIS

LOS ALAMOS QUALITY PROGRAM



APPROVAL FOR RELEASE

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Los Alamos
Yucca Mountain Site
Characterization Project

HISTORY OF REVISION

REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE
R0	01/06/92	N/A	Initial procedure.
R1	04/28/93	All	Major rewrite.
R2	08/16/96	All	Major rewrite to better clarify the process. Revisions R0 and R1 of this procedure were previously identified as LANL-INC-DP-95.

Los AlamosYucca Mountain Site
Characterization Project

PREPARATION OF SAMPLES FOR CHLORINE-36 ANALYSIS

1.0 PURPOSE

This detailed technical procedure (DP) describes the procedure used to process soluble chloride, either present in a water sample or leached from a soil or rock sample, into purified silver chloride precipitate in preparation for chlorine-36 (^{36}Cl) analysis by accelerator mass spectrometry. This work is part of the Water Movement Test task for the Yucca Mountain Site Characterization Project (YMP).

2.0 SCOPE

This DP applies to all YMP personnel who process aqueous samples in preparation for ^{36}Cl analysis as part of the YMP's Water Movement Test task for Los Alamos National Laboratory (LANL).

3.0 REFERENCES

LANL-YMP-QP-02.7	Personnel Training
LANL-YMP-QP-03.5	Documenting Scientific Investigations
LANL-YMP-QP-12.3	Control of Measuring and Test Equipment and Standards
LANL-INC-DP-88	Collection of Soil Samples for Analysis of Moisture Content, Bulk Density, Halides and Chlorine Isotopes
LANL-CST-DP-92	Sample Leaching to Extract Soluble Chloride and Bromide
LANL-CST-DP-93	Step-Leaching Procedure for Extracting Soluble Chloride and Bromide
LANL-CST-DP-94	Using Ion Chromatography to Determine Chloride and Bromide Concentrations
LANL-CST-DP-97	Preparation of Carrier Solution for Chlorine-36 Samples
LANL-CST-DP-103	Identification, Storage, and Handling of Samples for the Water Movement Test

4.0 DEFINITIONS

4.1 Water, Soil and Rock Samples

Water, soil and rock samples are materials intended for laboratory studies or analyses as part of Yucca Mountain site characterization activities. Soil includes any unconsolidated material above bedrock, i.e., the regolith, collected by the methods described in DP-88. Rock samples may include, but are not limited to, surface samples, drill cores, drill cuttings, and samples from mining operations.

4.2 Leachate

Leachate is the aqueous solution obtained as a result of combining reagent water with a sample of soil or rock and allowing time for soluble constituents to dissolve into the water, following procedures described in DP-92 and DP-93.

4.3 Reagent Water

Reagent water is water that has been analytically purified to remove impurities so that the resistivity is greater than 17.5 megohms.

4.4 Carrier

Carrier is a chloride salt, prepared in solution pursuant to DP-97, that contains a negligible concentration of ^{36}Cl relative to stable chlorine, i.e., the carrier has a $^{36}\text{Cl}/\text{Cl}$ ratio $\leq 5 \times 10^{-15}$. Carrier is used to prepare ^{36}Cl process blanks (see section 4.9) and may also be added to a sample in order to increase the chloride mass to levels sufficient for analysis by accelerator mass spectrometry.

4.5 Tracer

Tracer is a chloride salt that is a specific type of carrier in that it contains nearly pure chlorine-35 with only a negligible concentration of chlorine-37, in addition to a negligible concentration of ^{36}Cl . Tracer is used to prepare ^{36}Cl process blanks (see section 4.9) and may also be added to a sample in order to increase the chloride mass to a level sufficient for analysis by accelerator mass spectrometry. When used for the latter purpose, the analytical technique is known as isotope dilution mass spectrometry, and it also allows an independent measure of the chloride concentration of the sample.

4.6 Accelerator Mass Spectrometry

Accelerator mass spectrometry (AMS) is the analytical method used to determine the atomic ratio of ^{36}Cl to total chlorine in a sample of silver chloride. For isotope dilution mass spectrometry, the atomic ratio of chlorine-35 to chlorine-37 is also measured in the same sample.

4.7 Sample Suite

A sample suite results from the processing of several geologic or water samples in which the resultant silver chloride (AgCl) precipitates are prepared within a relatively short period of time (e.g., about two weeks). A suite of AgCl precipitates is usually submitted at the same time to the AMS facility for ^{36}Cl analysis. Each suite is accompanied by at least one chloride and ^{36}Cl process blank (sections 4.8 and 4.9).

4.8 Chloride Process Blank

The purpose of a chloride process blank is to test for the presence of chloride contamination in the materials used for processing samples for ^{36}Cl analysis. The chloride process blank consists of taking a volume of reagent water through the same processes, and using the same materials, as are used for actual samples, following DP-92 and this DP. The process blank is then analyzed for chloride following DP-94. Because the materials used in this process should be chloride-free, the detection of any chloride may indicate a problem with chloride contamination.

4.9 Chlorine-36 Process Blank

A ^{36}Cl process blank is used to test for ^{36}Cl contamination of the reagents and the laboratory environment used for processing samples for ^{36}Cl analysis following this DP. A sufficient amount of the ^{36}Cl -free carrier solution, plus a component of the tracer solution if desired (both prepared pursuant to DP-97), is added to the chloride process blank (section 4.8), which is then processed in an identical manner as is used for actual samples, using the materials and methods described in this DP.

4.10 Replicate Sample

The purpose of a replicate sample is to periodically assess the reproducibility of the $^{36}\text{Cl}/\text{Cl}$ AMS analysis. The replicate is prepared by splitting a single precipitate into two or more subsamples, each submitted to the AMS facility under a unique identifier.

5.0 RESPONSIBILITIES

The following personnel are responsible for activities in Section 6.0 of this procedure:

- Principal Investigator (PI)
- YMP Employee (User)

6.0 PROCEDURE

The use of this procedure must be controlled as follows:

- If this procedure cannot be implemented as written, YMP personnel should notify appropriate supervision. If it is determined that a portion of the work cannot be accomplished as described in this DP, or would result in an undesirable situation, that portion of the work will be stopped and not resumed until this procedure is modified, replaced by a new document, or current work practice is documented in accordance with QP-03.5, subsection 6.1.6.
- Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct

revision of this procedure is used.

- When this procedure becomes obsolete or superseded, it must be destroyed or marked “superseded” to ensure that this document is not used to perform work.

6.1 Principle

Soluble chloride in water samples and soil and rock leachate is precipitated as AgCl by adding a AgNO₃ solution. In preparation for analysis by AMS, the AgCl is purified by repeated dissolution in ammonium hydroxide (NH₄OH) and reprecipitation by acidification with nitric acid (HNO₃). Following this DP, the final AgCl precipitate should then be free of any sulfur impurities which could otherwise interfere with the AMS analysis.

Ideally, the quantity of AgCl submitted for AMS analysis is on the order of 15 mg or more. Quantities less than this amount may have an increased level of uncertainty associated with the analysis. If determination of the chloride concentration in the leachate or water sample indicates that the quantity of chloride present is less than the desired amount, then the user has three options. These options include, proceeding with the analysis of the sample as-is, adding carrier or tracer to increase the quantity of chloride for analysis, or leaching additional rock or soil material.

6.2 Equipment and Hardware/Software

6.2.1 Equipment Malfunctions

Any equipment malfunction occurring during implementation of this procedure is likely to be readily detectable in the course of conducting work and hence is not expected to have a detrimental effect on the final results. The water purification system has a meter that indicates the resistivity of the purified water. This meter is checked each time water is drawn to verify that the resistivity is an acceptable value, i.e., at least 17.5 megohms. If a problem with any equipment arises which can be considered a potential source of error or uncertainty for the results, then it is addressed following section 6.7.

6.2.2 Safety Considerations

Good laboratory and scientific practices are used in the laboratory to protect against injury. Applicable LANL and/or LANL-contractor safety practices for conducting laboratory work are followed, as appropriate. Several steps in this procedure must be conducted under a fume hood. Proper procedures are followed for disposal of hazardous chemical wastes, e.g., silver-bearing solutions.

6.2.3 Special Handling

Care must be taken to minimize any potential for contamination of the carrier or tracer solution with ^{36}Cl or Cl . Precautionary measures are described in sections 6.3 and 6.4.

6.2.4 Equipment, Materials and Chemicals

Equipment, materials and chemicals which may be needed to prepare samples for ^{36}Cl analysis are listed below. Required entries related to these items are listed in Attachment 1. Items equivalent to those listed below may be used provided they perform the same function with an acceptable level of performance as judged by the user or the PI.

6.2.4.1 Equipment

- water purification system capable of producing reagent water (e.g., Millipore Milli-Q Analytical Grade Deionizing Water Purification System, Model ZD20)
- analytical balance (e.g., Mettler Model AE 240)
- vacuum pump for filtration apparatus
- hot plate with temperature control up to 100°C or greater (e.g., Lindberg Hot Plate, Model 53015)
- centrifuge
- convection oven capable of maintaining the temperature at $85^{\circ}\text{C} \pm 10^{\circ}\text{C}$

6.2.4.2 Materials and Supplies

New labware is initially washed with detergent such as Alconox, rinsed with tap water, then rinsed three times with reagent water. Subsequent use requires rinsing three times with reagent water, unless excessive sample material or non-soluble compounds have contaminated a piece of labware, in which case the item is washed using the procedure for new labware. Just prior to use, each piece of labware is rinsed with a small volume of the solution it will contain.

A detailed list of materials and supplies is listed below. Alternative materials may be used provided that the user judges them to perform the same function with an acceptable level of performance. Not all of the following items may be necessary to complete the requirements of this DP.

- centrifuge tubes
- hot mitt or pot holder
- stir bars, large and small
- small-volume digital pipet or disposable transfer pipet for adding AgNO_3 and HNO_3
- large beakers or wide-mouthed flasks

- filtration apparatus or syringe
- 0.45 μm nylon syringe filters
- glass microfibre filters
- pre-rinsed 0.45 μm cellulose nitrate membrane filters (not Nucleopore brand, which may contain leachable chloride)
- forceps for picking up membrane filters
- small, amber-colored vials with Teflon lined caps
- permanent markers
- labeling tape
- aluminum foil
- parafilm

6.2.4.3 Reagent Chemicals

- reagent water
- high purity nitric acid (HNO_3), concentrated
- high purity ammonium hydroxide (NH_4OH), concentrated
- silver nitrate (AgNO_3) solution, between 0.05 and 0.5M
- barium nitrate ($\text{Ba}(\text{NO}_3)_2$), saturated solution
- carrier or tracer solution, prepared according to DP-97
- 200 proof ethyl alcohol

6.3 Preparatory Verification

6.3.1 Hold Points

For each suite of samples that is processed together for analysis by AMS, a chloride and ^{36}Cl process blank are prepared; the ^{36}Cl process blank and occasionally a sample replicate are submitted for analysis, usually but not necessarily at the same time as other samples in a given suite. The chloride process blank is prepared prior to processing of any samples in a given suite and tests for chloride contamination in the materials used for sample processing. The ^{36}Cl process blank is processed along with the actual samples in a given suite and tests for ^{36}Cl contamination in the chemicals and laboratory environment used for sample processing. The presence of chloride or ^{36}Cl contamination is a hold point and indicates that the leaching process or the sample preparation procedure may need to be modified by the PI or the user. These two hold points are described below:

6.3.1.1 Chloride Process Blank

The chloride process blank is prepared and analyzed in accordance with DP-92.

6.3.1.2 Chlorine-36 Process Blank

The ^{36}Cl process blank is prepared by adding to reagent water a sufficient volume or mass of carrier or tracer solution to contain about 1.5 to 5 mg Cl, following the protocol described in DP-97 for handling the carrier or tracer solution. The volume of reagent water should be approximately the same as used for leaching the samples that it accompanies. The blank is then processed in an identical manner as is used for actual samples. The resulting AgCl precipitate is analyzed for its $^{36}\text{Cl}/\text{Cl}$ ratio. This ratio should meet at least one of the following criteria: either the ratio is $\leq 5 \times 10^{-15}$ or the ratio is $\leq 5\%$ of the ratio measured for the sample with the lowest ^{36}Cl concentration among those in the same sample suite. If the ratio exceeds both of these threshold values, then the sample preparation procedure is potentially contaminating the samples and may need to be modified. The ^{36}Cl results for samples in a suite with a high ^{36}Cl process blank are reviewed by the PI for acceptability on a case-by-case basis.

6.3.2 Calibration

The analytical balances, which are used to weigh reagents and the final AgCl precipitate, are controlled pursuant to QP-12.3.

6.3.3 Environmental Conditions

AgCl is sensitive to light, and Cl in AgCl will volatilize as Cl_2 in the presence of sunlight and, to a lesser extent, fluorescent light. Therefore, the AgCl precipitates are shielded from light as much as possible during sample processing and storage. The final precipitates are stored in amber glass vials.

6.4 Control of Samples

It is imperative that sample identification and control be sufficient to trace a sample and its derivatives from its original field location to the point of analysis and that the integrity of the sample be safeguarded during the entire analytical process. Consequently, investigators must be trained to DP-103 before they can work with samples analytically and they must also follow guidelines set forth in that document for sample management.

Laboratory storage containers are labeled with the identifier of the sample that they are to hold, prior to that sample being transferred into them. This precaution will reduce the possibility of incorrect or ambiguous sample identification and cross-contamination.

6.5 Implementing Procedure

The user conducts the following steps. Attachment 1 lists the information that is required to be documented in a laboratory notebook for work conducted under this DP.

6.5.1 Adequacy of Sample Size

This step may be skipped for leachates if already conducted as part of DP-92 or DP-93, or if the sample is a ^{36}Cl process blank prepared from an aliquot of carrier or tracer solution.

6.5.1.1 Measured Chloride Quantity

An aliquot of the aqueous sample is analyzed for chloride and bromide, following DP-94. The total amount of chloride in the sample is estimated from the measured chloride concentration and the volume of sample.

6.5.1.2 Target Chloride Quantity

A minimum of 1.5 mg Cl (5 mg AgCl) is desired for ^{36}Cl analysis. However, 4 mg Cl (15 mg AgCl) is the recommended amount because the excess material can be used for a replicate analysis as a check on the reproducibility of the AMS result, or can be set aside for re-analysis in case the first result is in doubt. Because chloride is lost in the sample preparation process, 5 mg Cl (20 mg AgCl) is the suggested target amount.

6.5.1.3 Determination of Adequacy of Sample Quantity

If the total chloride in the aqueous sample is significantly less than 1.5 mg, the user may augment the recovered Cl by processing additional sample material; the two aqueous samples are then combined and processed as a single sample by this DP. Alternatively, the user may add an appropriate amount of tracer if available or ^{36}Cl -free carrier, prepared in solution pursuant to DP-97, to the aqueous sample to increase the quantity of Cl in the sample. The desired quantity of tracer or carrier is added, by weighing the solution.

6.5.1.4 Evaporation

The pH of the aqueous solution is adjusted to approximately 7, by slowly adding concentrated NH_4OH . If the volume of the solution is significantly greater than one liter, then it is evaporated down to one liter or less. With a neutral pH, the solution will not lose chloride by volatilization of hydrogen chloride. The final volume of the solution does not need to be determined.

6.5.2 Precipitation of Silver Chloride

6.5.2.1 Addition of Nitric Acid to the Aqueous Sample

To increase the ionic strength of the aqueous sample, high-purity HNO_3 is added to the sample at a concentration of 1 ml per liter of sample.

6.5.2.2 Addition of Silver Nitrate Solution

A weak solution of AgNO_3 (between 0.05 and 0.5 M) is used to precipitate the chloride present in the aqueous sample as AgCl . The quantity of AgNO_3 needed to precipitate the chloride present in the sample is first determined, and a slight (~ 10%) excess of this amount is added to the sample. The preferred form of AgCl precipitate is large, coagulated crystals. These are best acquired by adding the AgNO_3 slowly to a solution heated to steaming.

6.5.2.3 Cooling of the Solution

The aqueous sample is removed from the heat, covered, and placed in a dark place to cool for a minimum of one hour. Cooling the sample prior to transfer is important because it reduces the extent to which AgCl precipitate may be lost by dissolution in hot water.

6.5.3 Redissolution and Purification of Silver Chloride Precipitate

6.5.3.1 Centrifuge

The aqueous solution is decanted, and the AgCl precipitate is transferred as a slurry into one or more centrifuge tubes, which are then spun and the supernatant discarded. Under a fume hood, a minimum volume of NH_4OH (usually about 3 to 6 ml) is used to dissolve the AgCl and combine the AgCl into a single tube.

6.5.3.2 Water Bath Purification

The AgCl is then slowly reprecipitated using HNO_3 (usually about 3 to 5 ml) and placed in a hot reagent water bath for at least one hour. This step helps the AgCl coagulate and limits the quantity of impurities in the sample. The slurry is then centrifuged and the aqueous solution is decanted. The AgCl precipitate is again dissolved using a minimum volume of NH_4OH .

6.5.4 Removal of Sulfate Impurities

6.5.4.1 Addition of Barium Nitrate Solution

Sulfate is removed by adding 2 ml of saturated $\text{Ba}(\text{NO}_3)_2$ solution to the NH_4OH -AgCl solution. If sulfate is present, a whitish BaSO_4 precipitate will promptly begin to form. After addition of the $\text{Ba}(\text{NO}_3)_2$, the solution is stored in the dark for at least six hours.

6.5.4.2 Centrifugation

The solution is then spun in the centrifuge. If the user determines that sulfate impurities remain in the supernatant, then the supernatant is decanted into a new centrifuge tube. The user proceeds to step 6.5.5. However, if no further barium nitrate steps are needed to remove sulfate impurities, the solution is filtered through a $0.45\ \mu\text{m}$ filter which has been pre-rinsed using reagent water and NH_4OH . The user then proceeds to steps 6.5.5 and 6.5.6.

6.5.5 Reprecipitation of Silver Chloride

Working under a fume hood, the solution is acidified with a minimal quantity of high-purity concentrated HNO_3 (usually about 3 to 5 ml). Nitric acid is added by the drop until no additional white AgCl precipitate forms. The AgCl precipitate is then allowed to settle for at least one hour in a dark place. It is then centrifuged, and the aqueous solution is decanted and discarded. If deemed necessary by the user, the AgCl precipitate is redissolved using HN_4OH and steps 6.5.4 and 6.5.5 are repeated until any sulfate that is present has been removed.

6.5.6 Final Washing of Silver Chloride Precipitate

The AgCl precipitate is washed with reagent water in the centrifuge tube, and the supernatant is discarded after centrifuging. This water wash is repeated several times. A final wash is done using a minimal quantity of ethanol, and the supernatant is discarded after centrifuging.

6.5.7 Drying and Storing the Silver Chloride Precipitate

The AgCl precipitate is dried slowly in a convection oven at $85^\circ \pm 10^\circ\text{C}$. The dry precipitate is transferred to a pre-weighed or tared amber-colored vial and weighed on the analytical balance with a precision of 20%. The vial is labeled with the sample identifier following the protocol in DP-103.

6.5.8 Augmentation of Inadequate Quantity of Silver Chloride

Samples smaller than 5 mg can be analyzed by AMS if necessary although the analytical uncertainty increases as sample size decreases. Thus, the user has three options to deal with this problem: proceed with analysis of the sample as-is, process additional sample material (step 6.5.8.1), or add tracer or carrier (step 6.5.8.2).

6.5.8.1 Processing Additional Sample Material

The user may decide that additional soil or rock material should be leached following DP-92 or DP-93, with the leachate processed following steps 6.5.1 and 6.5.2 in this DP. The AgCl precipitate formed from this additional sample material is mixed together with the original AgCl by dissolving both in NH_4OH in step 6.5.3.1. The combined precipitates are processed following steps 6.5.4 through 6.5.7.

6.5.8.2 Addition of Carrier or Tracer to the Sample

As an alternative to step 6.5.8.1, the user may dilute the purified AgCl with a known, minimum amount of tracer or carrier solution prepared pursuant to DP-97. The original AgCl precipitate is first weighed and then dissolved in NH_4OH . The desired quantity of the tracer or carrier solution is added, by weight, to the NH_4OH solution. If AgCl begins to precipitate immediately, then sufficient NH_4OH is added to redissolve all of the AgCl. Once all of the AgCl is dissolved, then the user continues the purification process, starting with step 6.5.4 and ending with step 6.5.7.

6.6 Data Acquisition and Reduction

Masses are recorded with precisions as noted in Attachment 1. The acceptability and precision of the data will be evaluated by the PI, taking into account the precision of the instruments used as documented pursuant to QP-12.3. Attachment 1 lists the required data entries.

6.7 Deviations from the DP and Potential Sources of Error and Uncertainty

Careful labeling of containers reduces errors due to mislabeling. The possibility of sample contamination is reduced by working in a clean environment. The user is responsible for documenting deviations from this procedure in accordance with QP-03.5. If a problem arises which can be considered a potential source of error or uncertainty for the results, then it is also documented in the laboratory notebook in accordance with QP-03.5.

7.0 RECORDS

Records to be generated as a result of the proper execution of this DP are entries in laboratory notebooks and in the Sample Inventory Logbook. These records are controlled by procedures QP-03.5 and DP-103. A checklist for laboratory notebook entries required for this DP is provided in Attachment 1.

8.0 ACCEPTANCE CRITERIA

The criteria that show that this procedure has been correctly implemented are the records identified in Section 7.0. Chlorine-36 results produced from samples prepared by this DP are accepted only if a given suite of samples included a chloride process blank and a ^{36}Cl process blank. The reproducibility of results is tested by periodically submitting a replicate sample for isotopic analysis.

9.0 TRAINING

A prerequisite for this DP is to train to DP-103. Training for this DP requires formal on-the-job training. Training of personnel to this DP is documented pursuant to QP-02.7.

10.0 ATTACHMENTS

Attachment 1: Checklist of Laboratory Notebook Entries (1 page)

CHECKLIST OF LABORATORY NOTEBOOK ENTRIES

Initial descriptive information is entered in the laboratory notebook or logbook as required by QP-03.5 prior to starting a technical procedure and on a continuing basis as experimental and procedural changes dictate. These entries are:

- reference to this DP, including revision number
- unique identifiers for any calibrated equipment used to conduct this DP
- manufacturer and lot number of chemical reagents used in this DP

Additional information is entered into the laboratory notebook or logbook as appropriate. These entries are:

- date
- deviations from specified technical procedure (if any)
- problems (if any) which may pose a potential source of error or uncertainty for the results
- reagent chemical masses and solution volumes for any reagent solutions prepared for this DP (with precisions of 10%)

In addition to general entries, several parameters need to be recorded in order to evaluate the resulting data. These entries are:

- sample processed, listed by its unique identifier (following DP-103)
- estimated chloride content of leachate or water sample
- mass and solution identifier for any tracer or carrier solution added (recorded to a precision of 1%)
- mass of final, purified AgCl precipitate (with a precision of 20%)
- unique identifier for AgCl precipitate (following DP-103)